

SALT WEATHERING: INFLUENCE OF EVAPORATION RATE, SUPERSATURATION AND CRYSTALLIZATION PATTERN

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ABSTRACT

Micro- and macroscale experiments which document the dynamics of salt damage to porous stone have yielded data which expose weaknesses in earlier interpretations. Previously unexplained differences are found in crystal morphology, crystallization patterns, kinetics and substrate damage when comparing the growth of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4) versus halite (NaCl). The crystallization pattern of sodium sulphate was strongly affected by relative humidity (RH), while a lesser RH effect was observed for sodium chloride. Macroscale experiments confirmed that mirabilite (crystallizing at $\text{RH} > 50$ per cent) and thenardite (crystallizing at $\text{RH} < 50$ per cent) tend to form subflorescence in highly localized areas under conditions of constant RH and temperature. This crystallization pattern was more damaging than that of halite, since halite tended to grow as efflorescence or by filling the smallest pores of the stone in a homogeneous fashion, a result which contradicts Wellman and Wilson's theoretical model of salt damage. Low RH promoted rapid evaporation of saline solutions and higher supersaturation levels, resulting in the greatest damage to the stone in the case of both sodium sulphate and sodium chloride crystallization. At any particular crystallization condition, sodium chloride tended to reach lower supersaturation levels (resulting in the crystallization of isometric crystals) and created negligible damage, while sodium sulphate reached higher supersaturation ratios (resulting in non-equilibrium crystal shapes), resulting in significant damage. ESEM showed no damage from sodium sulphate due to hydration. Instead, after water condensation on thenardite crystals, rapid dissolution followed by precipitation of mirabilite took place, resulting in stone damage by means of crystallization pressure generation.

It is concluded that salt damage due to crystallization pressure appears to be largely a function of solution supersaturation ratio and location of crystallization. These key factors are related to solution properties and evaporation rates, which are constrained by solution composition, environmental conditions, substrate properties, and salt crystallization growth patterns.

When combined with a critical review of salt damage literature, these experiments allow the development of a model which explains variations in damage related to combinations of different salts, substrates and environmental conditions. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS salt weathering; environmental conditions; crystallization pressure; stone decay; sodium sulphate; sodium chloride

INTRODUCTION

Over the last few decades, many field and laboratory studies have shown that salt weathering is an important mechanism of rock decay in a range of environments (Evans, 1970; Pye and Sperling, 1983; Goudie, 1985; Trenhaile, 1987; Yatsu, 1988; Matsukura and Kanai, 1988; Cooke *et al.*, 1993; Goudie and Viles, 1997). Salt weathering is thought to play a role in the development of many geomorphologic features such as alveoles or honeycombs (Mustoe, 1982), tafoni or cavernous weathering (Bradley *et al.*, 1978) and pedestal rocks (Chapman, 1980). It is also considered to be an important contributor to the production of rock debris, especially in arid regions (Beaumont, 1968; Goudie, 1977; Goudie and Day, 1980), coastal areas (Mottershead, 1989) and in Antarctica (Prebble, 1967). Indeed, salt weathering may be a common planetary phenomenon, since Malin (1974) has suggested it could be responsible for some aspects of Martian landscapes (see also Clark and Van Hart, 1981; Clark, 1993). In addition, salt

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weathering of building stones is recognized as one of the primary agents in the loss of historic architecture (Evans, 1970; Winkler, 1973; Amoroso and Fassina, 1983; Smith *et al.*, 1988; Winkler, 1994; Cooke, 1994; Price, 1996; Cooke and Gibbs, 1995); and many structures in archaeological sites have also been damaged by this process (Lucas, 1925; Winkler, 1965; Goudie, 1977). Salts have had a significant impact on civil engineering, since they have been found to be responsible for damage to roads, highways, runways, dams and building foundations (Netterberg and Loudon, 1980; Sayward, 1984; Obika *et al.*, 1989; Doornkamp and Ibrahim, 1990; Goudie and Viles, 1997). In hot, arid areas, such as the Middle East, the full significance of salt weathering as an engineering hazard became evident after the construction boom of the 1970s and 1980s (Doornkamp and Ibrahim, 1990). Additionally, salt crystallization tests have been used since 1828 to evaluate the durability of construction materials (Evans, 1970; Price, 1978). However, recent debate as to the suitability of the standard sodium sulphate test for aggregate durability (ASTM, BRE) has also brought into focus our imperfect knowledge of this process (McMahon *et al.*, 1992). From the above it is obvious that salt weathering is not only of academic interest but, in some circumstances, it is a hazard with significant cultural and economic implications.

Nevertheless, while many researchers have studied this subject, the processes and pathways of salt damage are still poorly understood (Zehnder and Arnold, 1989; Doehne, 1994; Rodriguez-Navarro *et al.*, 1996). In fact, there appear to be many unverified assumptions as to how and why salt weathering occurs. This has led to some general, well accepted salt damage models that do not explain many observed phenomena. For instance, it is widely accepted that salts cause more damage to rocks containing a large proportion of micropores connected to macropores, because of thermodynamic assumptions that salts growing in the macropores have a lower free energy of formation and tend to be supplied with solution from the micropores. A theoretical model for this assumption was promulgated by Wellman and Wilson (1965). This notion appears to be well accepted in the literature (Fitzner and Snethlage, 1982; Zehnder and Arnold, 1989; Rossi-Manaresi and Tucci, 1991; Fitzner *et al.*, 1996), despite a paucity of detailed experimental observations as to where and how salts grow in porous materials, as well as how the resulting damage takes place. Furthermore, a clear explanation has been lacking for the contrasting damage potential of different salts. Many empirical studies have ranked the ability of various salts to cause damage to porous stones (Goudie and Cooke, 1970; Kwaad, 1970; Goudie, 1974, 1986, 1993; McGreevy and Smith, 1982). However, no convincing and experimentally verified answer yet exists to the following question: Why are some salts more damaging than others? In addition, there is little agreement on the importance of the various parameters contributing to salt weathering. For instance, some consider as more determinant the stone properties (McGreevy, 1996), others, the environmental conditions (Sperling and Cooke, 1985; Davison, 1986), while still others focus on the salt composition (Kwaad, 1970; Goudie, 1993). While all these variables have some significance, and studying each in isolation yields useful information, such studies may generate results that cannot readily be compared and may further complicate our lack of knowledge concerning the key parameters controlling salt weathering and the dynamics of this decay process.

To date, few studies have been performed on the dynamics (and the effects) of crystal growth within a capillary or a pore considering the particular crystallographic behaviour of each salt involved in the process of salt weathering. Zehnder and Arnold (1989) and Obika *et al.* (1989) showed that the crystallographic characteristics of a particular salt may control the pattern and degree of damage created when crystallization and growth take place within a pore. Thus, the morphology and growth rate of the newly formed salt crystals appear to be important keys to understanding this particular decay phenomenon. Sunagawa (1981) demonstrated that crystal shape and morphology are dependent on the degree of supersaturation reached when crystallization takes place, and this parameter is mainly controlled by the initial solution concentration and environmental/physical parameters such as temperature, relative humidity, surface area and roughness of the substrate. Thus, the physical properties of a salt solution (i.e. viscosity, surface tension and vapour pressure) will have a critical effect on the dynamics of solution flow and evaporation within the stone, and therefore on the degree of

supersaturation, the dynamics of precipitation and salt growth, and the resulting damage to porous host materials (Puehringer and Engstrom, 1985).

Another issue to be dealt with when addressing salt decay problems is the difference between the process of salt crystallization on the surface of a porous material (efflorescence) and the crystallization within the porous system (subflorescence). The former, while appearing impressive, typically results in little damage to the stone, whereas, by contrast, the latter typically creates extensive damage (Cooling, 1930). Certain salts are prone to effloresce, while others crystallize more readily inside a pore (Rodriguez-Navarro *et al.*, 1996), and it is important to understand why. Environmental changes (especially relative humidity) can promote changes in the location and/or in the way salt crystallization and growth take place, either promoting the formation of efflorescence or generating subflorescence.

Additionally, little attention has been paid to the fact that a liquid (salt solution) in a porous rock can reduce the mechanical strength of the rock. Dunning and Huf (1983) demonstrated experimentally that the presence of a liquid in the pores of a rock submitted to stress, greatly increased the rate of crack propagation. They explained this phenomenon as a reduction in the interfacial tension between rock minerals, due to wetting by the liquid. Walder and Hallet (1985) and Selby (1993) pointed out that stress corrosion cracking phenomena that occur in the presence of a liquid are important decay processes, which have received little attention in geomorphological literature. Thus, when considering the damage produced by salts, the crack-enhancing effects of the solution itself must be taken into account when salt crystallization or hydration pressures are generated. This means that a rock can experience considerable damage even if little pressure is exerted by the salts.

Considering the importance of this decay mechanism, not only from a geomorphologic point of view, but also from a cultural and economic standpoint, it is essential to reveal the fundamental mechanisms leading to salt damage, identify the key parameters controlling this process, and determine how a better understanding of salt weathering can lead to new methods of mitigating this problem in the fields of engineering and heritage conservation.

In this paper, we undertake a series of dynamic experiments to begin to resolve these problems by comparing the crystallization behaviour of two typical salts under conditions of low and high relative humidity. The existing theories and models suggested for this process are also critiqued by combining information from studies in geomorphology, conservation science and engineering. An analysis of the results reveals some key parameters which control salt damage of porous stone, how and where crystallization occurs and in what kind of pores, elucidates why sodium chloride is less damaging than sodium sulphate and, finally, permits a critical evaluation of existing salt weathering models and prompts suggestions for future research. This work finds that the supersaturation ratio, the kinetics of nucleation and salt growth, the influence of environmental conditions (such as relative humidity), and how and where supersaturation is reached in a porous support are important parameters in the salt damage process.

SALT WEATHERING: THEORIES AND MODELS

Several salt damage mechanisms and corresponding theoretical models have been postulated to explain the widespread damage observed in field and laboratory studies of the problem. Primarily, salt weathering has been reported to be due to the build-up of crystallization pressure against pore walls when salt nucleation and growth take place in a confined space (Evans, 1970). Correns (1949) postulated that a salt crystal can grow against a confining pressure (as demonstrated by the experiments carried out by Taber (1916) if a thin, supersaturated solution film is maintained at the salt–pore wall interface. The existence of the film is determined by the interfacial tension differences at the salt–solution, the salt–rock and the solution–rock interfaces. If the salt–rock interfacial tension is bigger than the sum of the other two terms, the solution can penetrate between the salt crystal and the pore wall, permitting the continued growth of the salt. The pressure is transmitted across the solution film, which may be semi-rigid under these conditions (Robin, 1978; Walder and Hallet, 1985). Correns (1949) proposed the following

equation which allows calculation of the pressure P (atm) exerted by a crystal growing from a saturated solution:

$$P = (RT/V_s) \ln (c/c_s) \quad (1)$$

where V_s ($\text{cm}^3 \text{ mol}^{-1}$) is the molar volume of the crystal substance, (c/c_s) is the ratio of actual to saturation concentration (supersaturation ratio), R is the gas constant ($\text{cm}^3 \text{ atm K}^{-1} \text{ g-mol}^{-1}$) and T is the temperature (K). On the basis of this equation, Winkler and Singer (1972), calculated the pressures potentially exerted by common salts and concluded that, under certain supersaturation states, the pressures generated by salts undergoing crystallization inside a pore could be high enough to disintegrate most commonly used porous building materials. This model has also successfully explained the 'displacive growth' of minerals such as pyrite in confined sediments (Carstens, 1986).

Weyl (1959) proposed a general model to understand the 'force of crystallization' of minerals as the opposite of the pressure solution process. This model considers Correns' model essentially as a special case. Weyl postulated that growth at a stressed crystal face requires the presence of a supersaturated solution film between the crystal face and its constraint. The thickness of this film, which is necessary for the diffusion of solutes to the precipitation site, was assumed by Weyl (1959) and Tada *et al.* (1987) to be of the order of several nanometres. The force of crystallization is the result of the deposition of matter on the growing crystal surface, at the crystal-pore wall interface. If the solution is supersaturated, precipitation in the area of contact between the crystal and the pore wall will take place if the ratio of the supersaturation to the stress coefficient of solubility is greater than the average normal stress between the crystal and the pore wall. If the stress is increased above this limit, pressure solution will take place. This model, in fact, explains the experimental results from Taber (1916) who observed that alum crystals grew faster under low pressure than under high pressures. Weyl (1959) provides different expressions that permit the forces of crystallizations to be calculated. This model, according to Evans (1970), is the only acceptable explanation for the observed force of crystallization (salt damage). Nevertheless, Yatsu (1988) criticized Weyl's model for its assumption that the concentration of solute at the crystal-rock film is a linear function of the effective normal stress across the film, since the validity of this assumption has not been verified. However, data from Tada *et al.* (1987), Maliva and Siever (1988) and Dewers and Ortoleva (1990) corroborate the validity of Weyl's model, and its applicability to explain various natural phenomena. A comparable model has been applied recently to explain frost weathering (Walder and Hallet, 1985, 1986).

Wellman and Wilson (1965) developed a thermodynamic model for calculating the crystallization pressure of a salt, considering that the free energy of a solid increases with its surface area. Thus, to keep the free energy of a system at a minimum, the area of its interfaces should tend to be minimized as well. The work required to be done during crystal growth on one face of the crystal is equal to $(P_l - P_s)dV$, where P_l is the pressure in the liquid, P_s is the pressure in the solid (in atmospheres) and dV is the increase of crystal volume (cm^3). This work should be equal to the work required to extend the surface, which is equal to σdA , where σ is the interfacial tension between the solution and the growing crystal (dyne cm^{-2}) and dA is the increase of crystal surface area (cm^2). σ is independent of V , therefore:

$$P_l - P_s = \sigma dA/dV \quad (2)$$

Wellman and Wilson (1965) concluded that salt crystallization will therefore take place initially in the larger pores (forming large crystals, growing at the expense of the smaller) from solution being supplied from the smaller capillaries. When the larger capillaries are filled, the crystals will not grow into the smaller ones because this will require a significant increase of surface area relative to the small volumetric increase, resulting in a large increase in the chemical potential of the crystal. Thus, the crystals in the large pores will continue growing, generating pressure against the pore walls and eventually resulting in damage to the host material. Wellman and Wilson (1968) proposed that the excess pressure, ΔP (in atmospheres) built up in a large pore when crystallization takes place is equal to:

$$\Delta P = 2\sigma(1/R - 1/r) \quad (3)$$

where R is the radius of the large pore connected by a capillary of radius r (cm). Thus, when ΔP exceeds the tensile strength of the rock, fracture of the material will take place. This suggests that rocks with large capillaries separated by areas of micropores are most susceptible to disruption by crystallization of salts. The Wellman and Wilson model is based on the theoretical freezing model developed by Everett (1961) who established that freezing results in the generation of 'capillary pressure' by a solid growing at the expense of a liquid in a capillary. However, the thermodynamic background for this theory, according to Evans (1980), is valid for gas-liquid and liquid-liquid interactions, but its use for solid-liquid interactions has not yet been validated. Moreover, Tiller (1991) stated that the 'capillary pressure', which is valid for liquids, is a fictitious quantity when applied to solids.

Several other salt damage mechanisms have been proposed and are still somewhat controversial: *hydration pressure* (Kwaad, 1970; Sperling and Cooke, 1985; Fahey, 1986; Charola and Weber, 1992; Doehne, 1994), *thermal expansion* (Cooke and Smalley, 1968; Chapman, 1980; Johannessen *et al.*, 1982), *chemical weathering* (McGreevy, 1985; Young, 1987; Mottershead and Pye, 1994), *osmotic pressure* (Winkler, 1970, 1994), and *hydraulic pressure* (McMahon, 1992). These mechanisms are assumed to have little relevance to the current experiments, for which crystallization due to evaporation appears to be the most important process. A general review of the problem of salt damage and its complexities can be found in the monograph by Goudie and Viles (1997).

MATERIALS AND METHODS

Stone type and properties

The damaging effects of salt crystallization within a naturally occurring porous medium were studied using an oolitic limestone (Monks Park stone, UK), which has been used in building construction for centuries (Leary, 1983). Previous experiments have shown that this stone is sensitive to salt decay (Schaffer, 1932, 1955; Honeyborne and Harris, 1958; Leary, 1983; Rodriguez-Navarro *et al.*, 1996). It is a fine-grained, homogeneous, buff-coloured stone. The oolites, which comprise *c.* 60–70 per cent of the stone, range in size from 300 to 600 μm , and are cemented by sparry calcite. Optical microscopy and scanning electron microscopy show that the stone has a high intergranular porosity concentrated mainly in the micritic oolites, and in the contact between the sparitic calcite crystals of the cement. The median pore radius is $0.25 \pm 0.05 \mu\text{m}$, and the average porosity is 20 ± 2 per cent as determined by mercury intrusion porosimetry (MIP). This limestone exhibits a small capillary suction coefficient (0.09 g cm^{-2}), slow capillary rise ($0.32 \text{ cm min}^{-1/2}$) and slow drying (determined according to RILEM, 1980). These characteristics may help determine the sensitivity of the stone to salt damage.

Microscale experiments

The aim of the microscale experiments was to study and determine the microscopic characteristics of salt crystallization and growth in both non-porous and porous media. Two salt solutions were chosen for this study: saturated sodium chloride (NaCl) and saturated sodium sulphate (Na_2SO_4) solutions. The crystal phases expected to develop were halite (NaCl) and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Eventually thenardite (Na_2SO_4) will form by mirabilite dehydration. These salts are well known for their presence in a wide range of locations and environments (Doorkamp and Ibrahim, 1990). Additionally, the two solutions allow comparison (in a narrow temperature range) of salt behaviour without hydrates (halite) and with different hydrated phases (thenardite–sodium sulphate heptahydrate–mirabilite).

Three sets of experiments were carried out. (i) Crystallization from a droplet of solution on a glass plate at different relative humidity (RH) conditions (20, 35, 50 and 65 per cent RH); (ii) crystallization within glass capillary tubes of different dimensions (50 μm up to 400 μm diameter): the course of these

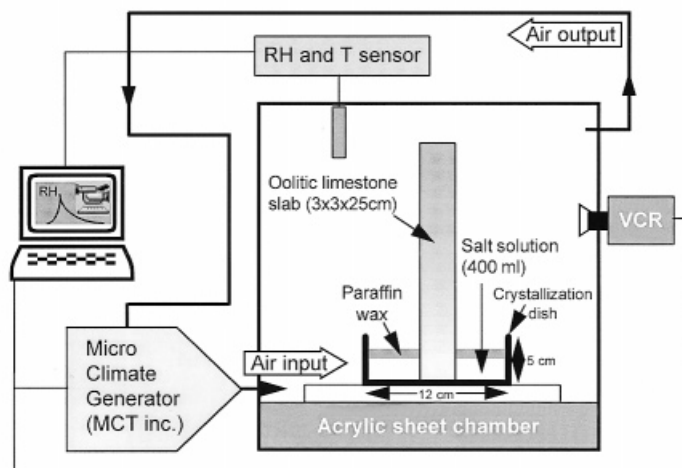


Figure 1. Macroscale salt experiment set-up for crystallization under contrasting RH conditions

two experiments was observed and documented at regular intervals via polarizing light microscopy and a computer-based, time-lapse video system. Phase analysis was performed by X-ray diffractometry (XRD, Siemens, model D5000). (iii) Crystallization of salts in a stone block observed by environmental scanning electron microscope (ESEM, Electroscan model E-3). An *in situ*, high magnification, dynamic monitoring of the crystallization process was performed in the ESEM chamber, with evaporation and/or condensation cycling, following the methodology developed by Danilatos (1993) and Doehne (1994). For studying the dynamics of crystal growth at high magnification, ESEM is a useful new tool because it allows the direct observation of the process of dissolution and precipitation of salts in porous supports (Doehne and Stulik, 1990; Doehne, 1994). Additional analyses of the salt crystals formed in stone blocks under varying RH conditions (macroscale experiments described below) were performed using the ESEM coupled with energy dispersive microanalysis (EDAX).

Macroscale experiments

The macroscopic characteristics of sodium chloride and sodium sulphate crystallization and growth within the oolitic limestone, and the resulting damage, were studied and evaluated. Stone blocks were partially immersed in a salt solution and, following capillary rise, crystallization occurred in the upper exposed stone areas (the 'wick effect', according to Goudie (1986)). The surface of the saline solution was covered with melted paraffin wax to promote the migration of the solution through the pore system of the stone, to avoid 'creeping' of the salt, and to minimize solution evaporation. Crystallization of the salt and the resulting damage took place under low RH (35 per cent) and medium-high RH (60 per cent) in a Micro Climate Technology (MCT) controlled environmental chamber. The temperature was kept constant at 20°C during all the experiments. No RH cycling or temperature variation was promoted during the experiment, thus, only continuous evaporation, supersaturation and salt crystallization were expected. Neither deliquescence of the existing salts followed by reprecipitation, nor any hydration process, would take place in such conditions. Figure 1 shows the experimental set-up which was intended to reproduce a common natural decay situation (Goudie, 1985, 1986), and at the same time to simulate a single damage process due solely to crystallization pressure.

The changes in appearance and salt morphologies were documented by means of a time-lapse video (TLV) system that recorded at a rate of one frame per minute. Details of the TLV system can be found elsewhere (Rodriguez-Navarro and Doehne, 1998). The extent of damage was evaluated by weighing the

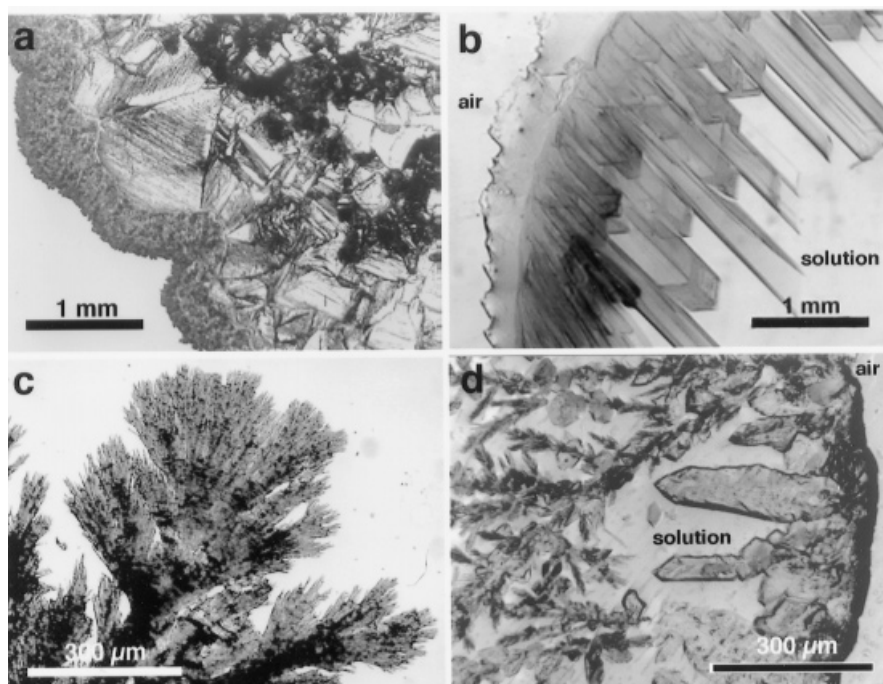


Figure 2. Optical microscopy micrographs of salt crystallization in a saturated solution droplet: (a) sodium chloride; (b) mirabilite growing at 60 per cent RH; (c) dendrite of mirabilite growing at the drop edge after dehydration of the crystals (high RH); (d) thenardite crystals growing inside the droplet at low RH

material that fell off of the stone surface (after salt removal by immersion in distilled water). Total weight loss was expressed as a percentage of the original weight of the stone block. The changes in porosity and pore size distribution, as well as the distribution of the salts in the decayed stones, were evaluated by means of mercury intrusion porosimetry. Samples of the unweathered stone, the stone submitted to salt weathering, and samples taken after salt extraction by immersion in distilled water were analysed using a mercury intrusion porosimeter (Micromeritic model 3300). Up to four replicate analyses were performed for each case. The evaporation rate of the two solutions under the two RH conditions mentioned above was determined by measuring the weight change of the beaker plus the stone block at constant intervals.

RESULTS

Microscale experiments

Crystallization from a droplet at different RH. Initially, NaCl crystallization always resulted in tiny euhedral, cubic crystals, which grew at the border and the centre of the droplet. In a second stage, mostly larger hopper crystals were formed at the edge of the droplet. Finally, massive skeletal and dendritic crystals grew at the outside of the edge of the droplet, and produced efflorescence-like precipitates (Figure 2a). This crystallization pattern was not affected by RH conditions. However, the number of well developed crystals was less numerous at the low RH.

At RH above 50 per cent sodium sulphate solution showed two stages of crystallization. First, prismatic euhedral mirabilite crystals grew within the limits of the droplet (Figure 2b). Second, acicular and dendritic aggregates of mirabilite were formed in the centre of the drop. In most cases, no appreciable dendritic growth was detected at the outside of the droplet at RH values higher than 50 per

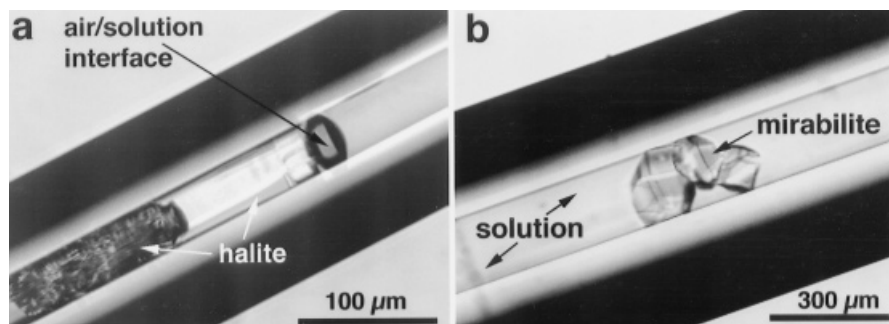


Figure 3. Optical microscopy micrographs of salt crystals growing in glass capillaries: (a) halite; (b) mirabilite

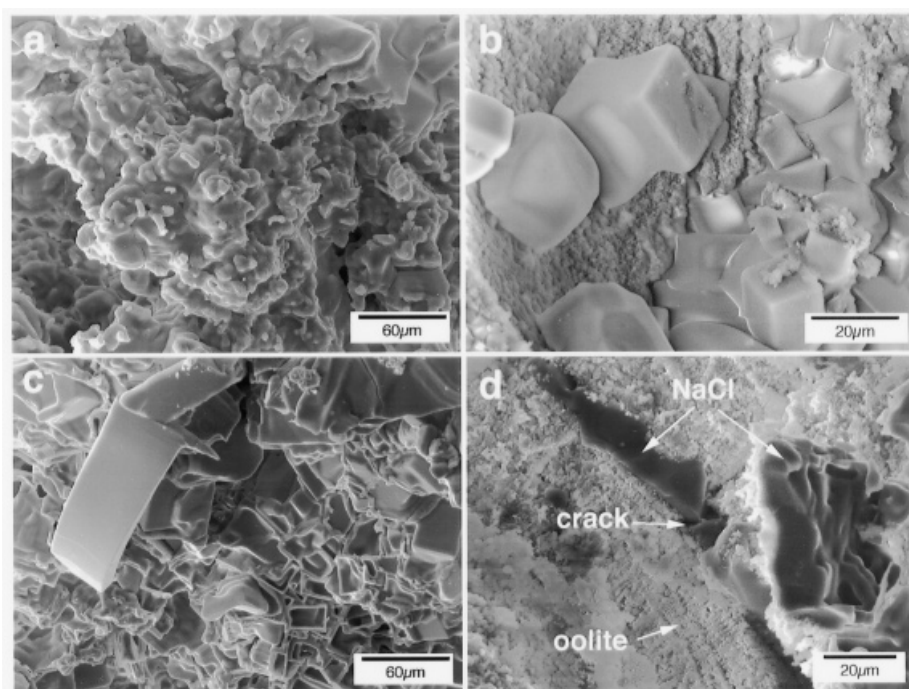


Figure 4. ESEM micrographs of waxy halite crystals filling micropores (a) and halite cubic efflorescence aggregates developed on the surface of the stone (b); prismatic, hollow-faced and hopper halite aggregates (c) and anhydrous halite crystals growing in fractures (d), developed at low RH conditions

cent. However, dendritic, branch-like crystals grew from the edges of the droplet in a small number of cases (Figure 2c). These crystals grew at the final stage of evaporation of the droplet, once the dehydration of mirabilite had begun. It should be noted that when dehydration of mirabilite occurred, the release of water of crystallization produced small, episodic pulses of water at the edge of the drop, which generated the secondary growth of efflorescence-like crystals outside the droplet. This is a well known phenomenon that was described by Washburn (1927) and Hazlehurst *et al.* (1936) and is considered to be responsible for the so-called 'creeping' of salt solutions.

In most of the experiments carried out at RH below 50 per cent, prismatic, acicular or bulky thenardite crystals (identified by XRD) grew inside the drop (Figure 2d). Thenardite crystals grew directly from the solution and they were not formed from dehydration of mirabilite. Crystallization at 20 per cent RH resulted in the formation of either euhedral, rhombohedral thenardite crystals (identified by

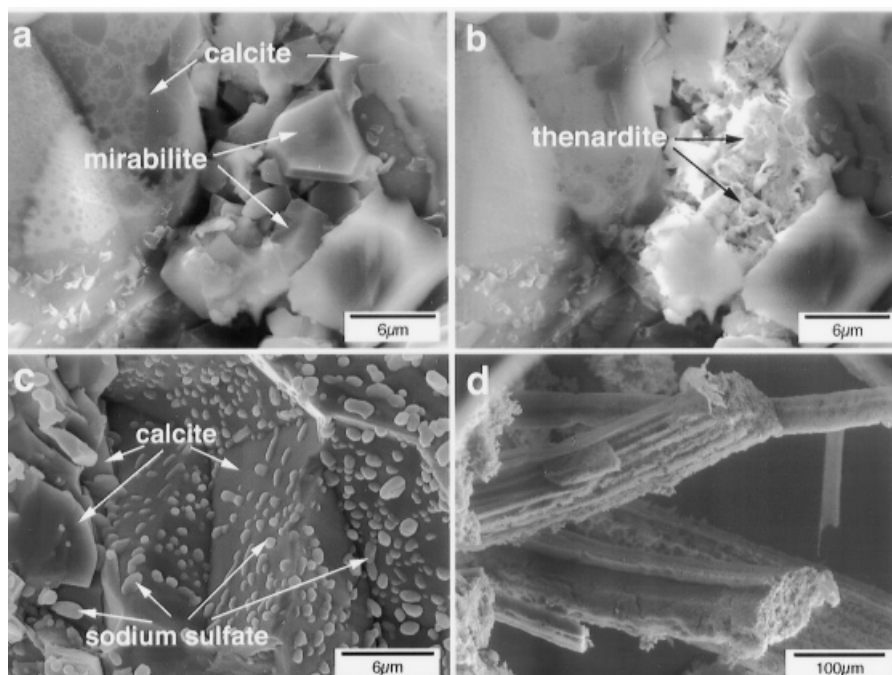


Figure 5. ESEM micrographs of sodium sulphate growing in a microcrack before (a) and (b) dehydration. Micrometre-sized sodium sulphate crystals (thenardite?) developed in fractures and on the faces of spalled sparitic calcite grains (c). Whisker-like sodium sulphate crystals (mirabilite) during dehydration (d)

XRD) or of large prismatic or hexagonal crystals. The latter crystals underwent a very slow dehydration (when compared with mirabilite) and were, presumably, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, a metastable phase reported by Sperling and Cooke (1985). However their identification by XRD was not successful.

Crystallization within capillary tubes. Halite crystals usually grew at the air–solution interface. Typically, a single large crystal was found on the surface of the solution plugging the capillary (Figure 3a). In contrast, a large number of crystals of mirabilite, with size equal to the capillary diameter, grew inside the solution (Figure 3b). No mirabilite crystals were found growing at the air–solution interface.

ESEM study. The dynamic ESEM study of the sodium chloride crystallization process showed that halite tended to grow within the pores of the stone as micrometre-sized, smooth-faced or waxy crystals filling the smaller capillaries and cementing the micritic calcite grains (Figure 4a). Halite was also seen as large euhedral cubic efflorescence aggregates on the surface of the stone (Figure 4b). The presence of micrometre-sized, halite crystals within the smallest pores of the stone (within the micritic oolites) was confirmed by EDAX microanalysis, and seems to be quite common (Eswaran *et al.*, 1980; Obika *et al.*, 1989). The rate of halite precipitation and growth within the pores of the stone was very slow (minutes). According to data from Sunagawa (1981), the cubic euhedral halite crystal morphology results from precipitation at low supersaturation ratios.

Samples collected from the stone submitted to sodium chloride crystallization in the environmental chamber (macroscale experiments) showed the same type of crystals developed in the ESEM experiments. However, after sodium chloride crystallization at 35 per cent RH, hollow-faced, hopper and prismatic halite crystals were found (Figure 4c). The latter morphologies may indicate slightly higher supersaturation ratios (Attolini *et al.*, 1986). Additionally, at low RH, some halite crystals were found growing inside fractures, specially at the oolite–cement interfaces (Figure 4d). At high RH conditions, halite tended to grow as perfect, smooth-faced cubic crystals, mainly as efflorescence or as waxy, micrometre-sized aggregates filling the stone pores.

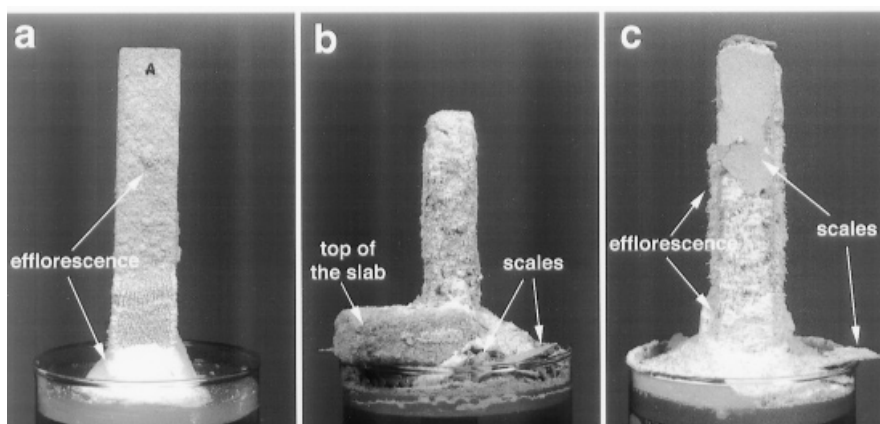


Figure 6. General view of the limestone blocks: (a) after sodium chloride crystallization at low RH; (b) after sodium sulphate crystallization at 35 per cent RH; (c) after sodium sulphate crystallization at 60 per cent RH

Table I. Weight loss (ΔW) and porosity of limestones after salt crystallization text

Salt	RH conditions (%)	$\Delta W^*(\%)$	Porosity (%) with salt	Porosity (%) without salt
NaCl	60	0.68	8.8	19.3
35	2.67	10.3	21.9	
Na ₂ SO ₄	60	7.06	20.2	20.5
	35	21.43	21.4	20.8

* $\Delta W = 100(W_0 - W_1)/W_0$, where W_0 is the initial weight and W_1 is the weight of the salt-free decayed sample

Mirabilite growth from solution within the stone was extremely rapid (almost instantaneous), resulting in three different morphologies. (i) Inside the pores, tiny anhedral or euhedral, plate-like and prismatic mirabilite crystals developed (Figure 5a), evolving into flake-like thenardite crystals once dehydration took place (Figure 5b). The growth of these crystals resulted in the formation of cracks within the sparitic calcite crystals cementing the oolites. (ii) In some cases, the development of anhedral, micrometre-sized sodium sulphate crystals was observed at the oolite–cement interfaces, or at the contact between sparitic calcite grains (Figure 5c). The growth of these crystals, which are probably thenardite crystals since no dehydration features were observed, resulted in the detachment of the oolites and the development of fractures within the calcite cement. The same type of crystals were observed in the delaminated stone scales collected from the macroscale experiments run at low RH conditions. After a second condensation and evaporation cycle in the ESEM, dissolution of the thenardite crystals took place, followed by precipitation of mirabilite crystals. No hydration of thenardite to form mirabilite was observed. (iii) Both on the internal faces of *c.* 2 mm up to *c.* 3 mm thick delaminated stone scales (collected from the macroscale experiments) and on the external surface of the stone, large ‘whisker-like’ crystals were found (Figure 5d). These ‘whiskers’, which were abundant on the surface of the stone submitted to salt decay at high RH, grew very slowly (*c.* 3 mm per day, as observed by the TLV recording), and generally after the scales were formed. This contributed to the mechanical separation of scales from the undamaged stone and eventually resulted in their falling off the stone. According to Sunagawa (1981), anhedral or non-equilibrium crystal habits indicate high supersaturation ratios. This is the case of morphologies (i) and (ii). Zehnder and Arnold (1989) reported the growth of euhedral and whisker-like salt crystals (corresponding to morphology (iii) in our experiment) at low supersaturation ratios.

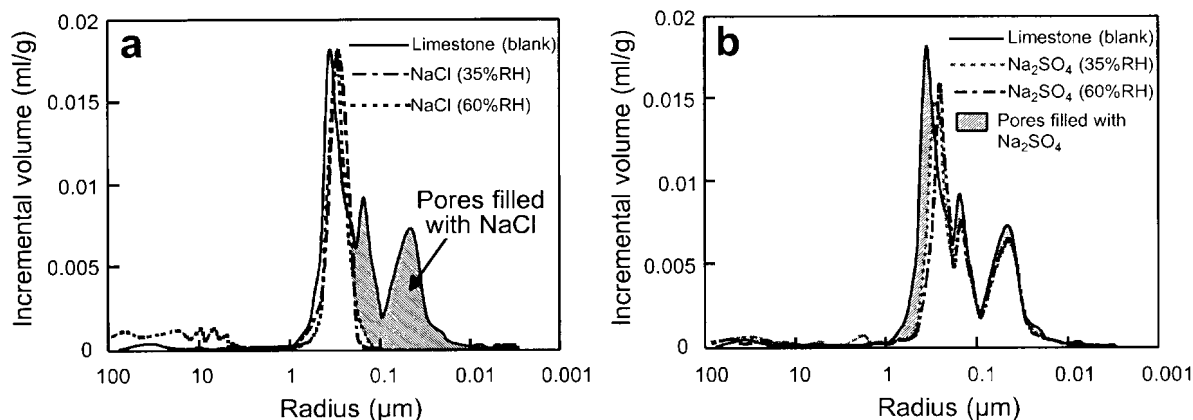


Figure 7. MIP data of limestone before and after crystallization of sodium chloride (a) and sodium sulphate (b) at different RH conditions (data collected before salt removal)

Macroscale experiments

Table I shows the average weight loss and porosity values for the macroscale experiments (data collected at the end of the experiment, which lasted 30 days). Regardless of RH conditions, an impressive volume of efflorescence covered the faces of the stone in which NaCl crystallization occurred (Figure 6a). Little damage, mainly due to powdering of the stone surface, was observed in these blocks. However, the stone submitted to sodium chloride crystallization at low RH showed granular disintegration and thin (less than 0.5 mm thick) scale formation when salt efflorescence was removed by immersion in distilled water. Massive loss of scales (more than 2 mm in thickness) and stone surface without development of noticeable efflorescence was observed in samples where sodium sulphate crystallization occurred at low RH. One sample was almost totally destroyed after 30 days from the start of the experiment (Figure 6b). Curiously, the shape of the top of the damaged block was rounded (probably resembling the shape of the capillary fringe). In comparison, large amounts of efflorescence and less weight loss were observed when crystallization took place at a relative humidity of 60 per cent (Figure 6c). Mercury intrusion porosimetry (MIP) of both surface and core samples of the stone submitted to NaCl crystallization shows an important porosity reduction, due to the filling of the smallest pores (Figure 7a). MIP analysis of both superficial and core samples collected after sodium sulphate crystallization shows little change when compared with the blank stone sample (Figure 7b).

As a general trend, and under similar conditions (temperature, RH, experimental set-up and stone support), it was observed that at the beginning of the experiment the evaporation rate of sodium sulphate solution was slower than the evaporation rate of sodium chloride solution (Figure 8). However, after some days the evaporation rate of NaCl solution was steadily reduced, indicating that the pores were filled with precipitated halite crystals, somehow preventing further damage (cementing action). Both NaCl and Na₂SO₄ solution evaporated faster at low RH than at high RH (Figure 8). Therefore, under constant capillary rise, the highest supersaturation ratios should occur at low RH.

Thenardite crystals may form at low RH, as shown by the experiments on crystallization from a solution droplet. Kwaad (1970) and Sperling and Cooke (1985) reported greater crystallization pressure, and damage, for thenardite crystallization than for mirabilite crystallization. However, it was not possible to identify which sodium sulphate phase was responsible for the initial damage to the stone. After collection of the salts found in lost scales, only thenardite was present (XRD data), but if mirabilite was the original salt, dehydration may have occurred since the experiments were run at RH below the transition point between thenardite to mirabilite, which is given as 71 per cent at 20°C by Arnold (1976). Only in the case of whisker growth was mirabilite identified. However, a few minutes after the collection of these latter crystals, dehydration and transformation to thenardite were observed.

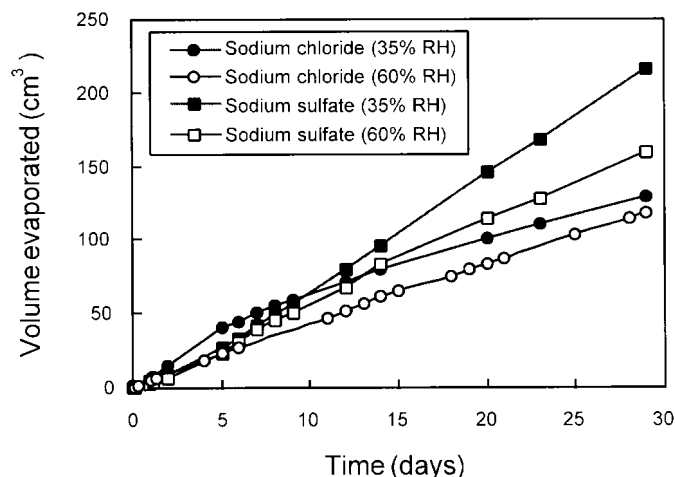


Figure 8. Evaporation rate from a limestone slab for NaCl and Na₂SO₄ saturated aqueous solutions at different RH conditions

DISCUSSION

Important and significant differences have been found in the crystallization and growth patterns of sodium chloride and sodium sulphate that may contribute to the extreme difference in damage potential commonly observed for these salts. Growth in solution droplets and in capillary tubes shows that halite tends to grow as perfect cubic crystals (initially forming inside the droplet), while the larger volume of material crystallizes as hopper crystals or as efflorescence-like, dendritic aggregates generally at the air–solution interface. In contrast, mirabilite (high RH conditions) and thenardite (low RH conditions) tend to grow *within* the solution as single, fast-growing prismatic, well developed crystals. However, at high RH condition, mirabilite sometimes develops dendritic aggregates outside the solution droplet. This may indicate that halite is prone to form efflorescence (air–solution interface) while mirabilite and thenardite are prone to form subflorescence (within the solution).

Under similar environmental conditions and using the same stone type, it was observed that negligible (high RH conditions) or little (low RH conditions) damage took place from halite growth. However, impressive damage occurs due to mirabilite and thenardite growth. Halite forms a large volume of efflorescence, and within the stone this salt is found filling the micropores in a uniform fashion. In the case of massive damage due to mirabilite/thenardite growth, little efflorescence growth was detected (under low RH conditions). Sodium sulphate was not homogeneously distributed through the stone pore system. No appreciable quantities of sodium sulphate were found filling stone pores (MIP results), but a high concentration of salt was found in a very narrow layer at the subsurface of the stone, where scales were formed and had been detached. At high RH, mirabilite growth results either in the development of efflorescence or the formation of scales, but with relatively less damage. However, the damage was still much greater than in the case of halite.

Sodium chloride versus sodium sulphate

Halite has been found to be responsible for salt damage in many locations and in many rock types (Evans, 1970; Chapman, 1980; Winkler, 1994). Nevertheless, in a large number of laboratory tests in which the effects of different salts were compared, NaCl crystallization produced little damage when compared with other salts, such as alkali metal sulphates, carbonates or nitrates (Kwaad, 1970; Goudie and Cooke, 1970; Smith and McGreevy, 1983, 1988; Goudie, 1986, 1993).

In the case of sodium sulphate, it should be noted that the high damage potential of this salt is a well documented observation that has been discussed by many authors (e.g. Schaffer, 1932; Evans, 1970;

Marschner, 1978; Price, 1978; Cooke, 1979; Sperling and Cooke, 1985; Goudie and Viles, 1997). This damage potential has led to the widespread use of this salt for testing the durability of building materials (Price, 1978). However, according to many authors (Kwaad, 1970; Charola and Weber, 1992; McMahon *et al.*, 1992; Doehne, 1994) the exact mechanism of sodium sulphate-induced decay is still not well understood. Cooke (1981) concluded that sodium sulphate is so damaging because: (a) sodium sulphate undergoes a high degree of volume change when hydrated; (b) sodium sulphate suffers a decrease of solubility at temperatures above (slow decrease) and below (rapid decrease) 32.4°C; (c) sodium sulphate is very soluble, thus a substantial quantity of solid salt is available for crystals to grow when evaporation takes place; and (d) the needle-shaped nature of sodium sulphate crystals might tend to increase their destructive force due to the crystallization pressure being concentrated over a smaller surface area.

Like Cooke (1981), Winkler (1973), Goudie (1977) and Marschner (1978) assumed that most of the damage attributed to this salt was caused by hydration pressure generated by the volume expansion as thenardite is hydrated to form mirabilite. However, no hydration took place in our experiments since the temperature and RH were kept constant. Only crystallization and growth (followed by eventual dehydration of mirabilite to form thenardite) took place, and still the damage was impressive. Additionally, no cooling or heating took place, and the solubility of Na₂SO₄ at 20°C (experimental conditions) is smaller than that of NaCl (16.1 weight per cent vs. 26.4 weight per cent respectively). Thus, most of Cook's hypotheses for the high damage potential of sodium sulphate do not explain our experimental results.

It seems likely that explanations for the extreme differences in damage potential between sodium sulphate and sodium chloride are associated with the differential crystallization pattern and growth kinetics of the two salts, as well as the solution physical properties (surface tension, vapour pressure and evaporation rate).

Influence of crystallization pattern on salt weathering

Mirabilite and thenardite tend to precipitate inside the solution creating subflorescence within the pores of the stone, while halite tends to precipitate at the air–solution interface, preferentially creating harmless efflorescence growing on the stone surface. However, MIP and ESEM data show that halite can also fill the micropores of the stone, while causing little evident damage. These results appear to conflict with the Wellman and Wilson (1965) theory for salt crystallization, since according to this theory, salts should grow in the larger pores, while in this experiment halite grew in the smallest. There does not seem to be a clear explanation for the negligible damage generated by the growth of halite inside the smallest pores, but it seems that low supersaturation ratios reached before NaCl nucleation, and a slow rate of halite precipitation and growth (observed in the ESEM), may hinder the build-up of enough pressure to damage the stone. As observed in the experiment carried out by precipitation on a glass plate, halite was observed to grow both at the edge of the droplet (a process which may induce efflorescence growth on a porous support) as well as in the centre of the drop (which may result in halite precipitation filling the smallest capillaries in a stone). It was generally observed that cubic halite crystals grew both inside the solution droplet as well as in the pores of the stone (macroscale experiment and ESEM microscale experiments). This crystal shape, according to data from Sunagawa (1981), corresponds to halite precipitation at low supersaturation. This implies that the crystallization pressure generated by this salt should be small (Correns, 1949; Winkler and Singer, 1972).

Eswaran *et al.* (1980) observed halite as cubic crystal aggregates in most saline crust in soils, reporting that hair-like or acicular halite crystals appeared only where the evaporation rates were extremely high. Obika *et al.* (1989) reported that significant damage to roads by sodium chloride is only observed when prismatic or acicular halite crystals occur, with these crystals growing at very high supersaturation ratios. Therefore, it can be hypothesized that according to the model proposed by Weyl (1959), under the low supersaturation ratios of our experiments halite crystals cannot generate enough pressure to produce the breakdown of the stone, and crystal growth should stop or else pressure-induced dissolution would take

place. It seems that a high supersaturation cannot be sustained in NaCl solution in the presence of a large surface area (pore walls) for heterogeneous nucleation to take place. Since growth occurs preferentially at the air–solution interface or at the interface with a solid, nucleation should be easy at low supersaturation. However, in some instances, it was observed that prismatic and hopper halite crystals were formed when crystallization took place at low RH. Under this condition, damage due to halite growth, while small if compared with sodium sulphate crystallization, was indeed more evident than in the case of halite growth at high RH. These observations confirm that low RH conditions promote higher supersaturation ratios with the result that halite can generate damage when it grows in non-equilibrium forms.

From dynamic ESEM crystallization experiments it is observed that mirabilite can grow very rapidly even in the smallest capillaries. Salt crystal morphologies indicate that sodium sulphate crystallization generally takes place at very high supersaturation ratios. This may be due to the presence of a wide metastable zone between saturation and the maximum supersaturation that sodium sulphate solutions can reach before crystallization begins (Winkler and Singer, 1972). In the case of sodium chloride it seems that this metastable zone is reduced. This factor seems to be an important contributor to the differential damage of both salts.

To explain the ability of these salts to create damage, it should also be considered that the presence of saline solution while crystals precipitate enhances crack propagation (as discussed by Dunning and Huf (1983) and Selby (1993). Additionally, in the case of sodium sulphate, after the crack is generated and dehydration of mirabilite to form thenardite is completed, a second condensation–evaporation cycle may result in the dissolution of the already formed sodium sulphate crystals, and the precipitation of new mirabilite crystals that generate additional damage. This experimental result suggests that hydration pressure is not an active mechanism in this decay process. Crystallization pressure appears to be the only mechanism generating stone weathering in our experiments.

Effect of relative humidity and physical properties of the saline solutions

Important differences in damage level were found after crystallization of sodium sulphate under varying RH conditions. Efflorescence growth, occurring essentially at high RH, produces less damage than subflorescence growth, which takes place mainly at low RH. This may be explained partly by (i) differences in evaporation rate (and supersaturation reached) and (ii) differences in the phase formed.

- (i) Low RH conditions will enhance the evaporation rate of the saline solution. Because the capillary rise is constant, since it depends on the solution surface tension, contact angle, viscosity and the pore radius – values that are constants for a given salt solution and stone type – an increase of the evaporation rate means that the solution will not reach the stone surface, but will evaporate below the stone surface. In fact, it was observed that the contour of the stone's damaged surface corresponds to a convex surface that may be representative of the limits of the capillary fringe. Cooke (1994) reported that under natural conditions salt weathering was concentrated at the limits of the capillary fringe, where high supersaturation is reached rapidly. Hence subflorescence, and damage resulting from high crystallization pressures (due to high supersaturation), will be promoted.
- (ii) On the other hand, at low RH direct precipitation of thenardite is observed (in the droplets), and the crystallization pressure of thenardite is greater than that of mirabilite for equal supersaturation ratios (Winkler and Singer, 1972). Thus, thenardite may promote greater damage than mirabilite, as observed also by Sperling and Cooke (1985) and Fahey (1985). However, it is not clear which factor is determinant, i.e. the high supersaturation ratio reached by rapid evaporation, or the crystallization of thenardite instead of mirabilite. Perhaps both act together at low relative humidity.

The slow capillary flow rate of saturated sodium sulphate solution allows evaporation to occur faster than the rate of replenishment of the solution by capillary migration from the inside of the stone. This will result in rapid supersaturation and subsequent damage due to salt crystallization under the stone's surface (Lewin, 1981). In contrast, sodium chloride saturated solution, having faster capillary rise (at

Table II. Comparison between key physical properties of sodium chloride and sodium sulphate saturated solutions. Data source: Lide (1996). Surface tensions measured by the authors (DuNouy Tensiometer, model CSC No. 70535)

Saturated solution*	Concentration (weight %)	Density (g cm ⁻³)	Surface tension (Pa)	Viscosity (mPa s)	Vapour pressure† (kPa)	RHeq (%)
NaCl	26.41	1.1978	8.35	1.986	1.7634	75.4
Na ₂ SO ₄	16.13	1.1503	7.66	1.812	2.1750	93‡

* All values at 20°C

† Vapour pressure of distilled water at 20°C is 2.3388 kPa

‡ Data from Price and Brimblecombe

least at the beginning of the experiment, before plugging of the micropores takes place), will be prone to evaporate at the surface of the stone, precipitating mainly as efflorescence. The differential flow behaviour of the two saline solutions is due mainly to the higher surface tension of the saturated sodium chloride solution, compared with the saturated sodium sulphate solution (Gummerson *et al.*, 1980; Garrecht *et al.*, 1991). Once the solutions reach the evaporation front (located at or below the surface of the stone), the evaporation rate will depend on the solution vapour pressure. Because the vapour pressure is higher in the case of sodium sulphate solution, faster evaporation will occur and the supersaturation ratio will be higher than in the case of sodium chloride solution, resulting in higher crystallization pressures. Pertinent physical properties of the two solutions are given in Table II.

Crystallization of sodium sulphate solutions at medium-high RH (60 per cent) results in the development of massive efflorescence and relatively little damage. This may be due partly to the ability of mirabilite to develop dendritic efflorescence-like crystals at the edges of the solution droplet at high RH, and because the solution replenishment towards the stone faces may be faster than the evaporation rate. Thus, due to the slow evaporation, low supersaturation will be reached and precipitation of the salt will take place mostly at the surface of the stone.

Sodium chloride can also generate more damage at low RH conditions. As in the case of sodium sulphate, rapid evaporation can induce the growth of subflorescence. Under these conditions, high supersaturation ratios can be reached before halite crystallization begins. Thus, enhancing the evaporation rate appears to increase the damage potential of this salt. According to Sperling and Cooke (1985), crystallization of salts and the resulting high crystallization pressures are favoured by rapid evaporation, thereby increasing the supersaturation of the solution. Rapid evaporation is enhanced by low RH, high temperature and wind flow. However, even at low RH conditions, the amount of damage due to halite growth is much less than that for sodium sulphate. In fact, halite efflorescence growth is dominant even at 35 per cent RH. These results show that differences in solution physical properties and crystallization patterns between sodium chloride and sodium sulphate can be responsible for their contrasting weathering properties.

Influence of the stone pore system

The following observations should be considered in order to evaluate the influence of the pore system characteristics on stone decay due to salt weathering: Schaffer (1932) demonstrated that stones with a high proportion of micropores were more susceptible to salt decay than those with high proportions of large pores. This fact has been confirmed by several studies (Honeyborne and Harris, 1958; Fitzner and Snethlage, 1982). Punuru *et al.* (1990) developed a model for durability factor calculations of natural stone based on the pore size distribution. They found that stones having a large number of pores with radii less than 0.5 µm were less durable than others. Wellman and Wilson (1965) offered a thermodynamic model aiming to explain these observations. However, our experimental results imply that a reduction of the solution flow rate by the presence of micropores is partly responsible for the increase of damage in this type of stone, because slow solution flow will result in the crystallization of the

salt deep under the stone surface. In fact, the hydric properties of a particular stone can be used to predict its resistance to salt decay phenomena (Honeyborne and Harris, 1958; Everett, 1961), since porosity and pore size distribution are the principal factors controlling the uptake and transport of liquid within a stone (Vos, 1976). The Wellman and Wilson model for salt decay does not take into account that, according to the Laplace and Washburn equation, the capillary (suction) pressure P (atm) is inversely proportional to the pore radius:

$$P = 2\sigma \cos\theta/r \quad (4)$$

where σ is the interfacial tension and θ is the contact angle of the meniscus at the pore wall of radius r (cm). This means that as evaporation progresses, the saturated solution will be suctioned from the larger pores towards the smaller ones, where it will concentrate. Thus, once a critical supersaturation is reached, crystallization will take place in the smaller pores, not in the larger ones. The larger pores will act as reservoirs supplying solution to the smaller ones where high supersaturation ratios can be reached. Tiller (1991) reported that heterogeneous nucleation of a crystal will occur in the smallest pores, where the solution will be withdrawn and eventually reach very high supersaturation ratios (thus generating high crystallization pressures, according to Correns, 1949).

The two factors discussed above may explain why stones with a high proportion of micropores connected to large pores are very susceptible to salt weathering. Micropores are very common in Monks Park limestone. Our experimental results confirm that these micropores result in a larger surface area for evaporation and slower solution transport, thus increasing the chances that high supersaturation ratios will be reached below the stone surface. In stones with larger pores, capillary rise is limited, surface area is lower, and solutions will reach the surface more readily, without achieving a high supersaturation, and resulting in efflorescence growth.

CONCLUSIONS

The extent of salt damage in porous stone due to crystallization pressure appears to be largely a function of solution supersaturation ratio and the location of crystallization. These key factors are in turn related to important properties and parameters, such as salt type and evaporation rates. Based on the experiments presented here, differential damage behaviour between sodium chloride and sodium sulphate appears largely to be due to differences in crystallization patterns, dynamics, and the location of the precipitates. Solution physical properties (e.g. surface tension and vapour pressure), environmental factors and pore-system characteristics of the stone support play key roles in determining the flow rate and evaporation rate of the saline solution and thus the resulting supersaturation ratio at the moment of crystallization. Combination of these factors determines whether crystallization will result in damaging subflorescence or almost harmless efflorescence. Furthermore, the dynamics and kinetics, as well as the crystallization pattern of each salt, will determine the location of the salt crystals, the crystallization pressure, and therefore the resulting damage.

The Wellman and Wilson (1965) model for salt damage does not seem to explain our experimental observations. However, our experimental results are in agreement with the original model for generation of crystallization pressure proposed by Correns (1949), and completed by Weyl (1959).

Nevertheless, for a better understanding of salt weathering processes, additional work needs to be done to verify our observations using other salt types (and mixtures), stone types and environmental conditions (RH, temperature ranges/cycles, and air flow). In particular, the crystallization pattern of salts and the kinetics of the salt crystallization process should be considered in detail in future studies. These studies should also include tests to evaluate the significance of cycling (i.e. crystallization/dissolution and/or hydration/dehydration cycles) and fatigue or threshold effects on salt weathering. Development of a model that can be used to explain the structure of some natural weathering forms and their weathering rates, as well as the degradation modes and rates of archaeological and architectural

stone affected by salt weathering, will be of importance in the design of conservation procedures for the protection of our cultural heritage.

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